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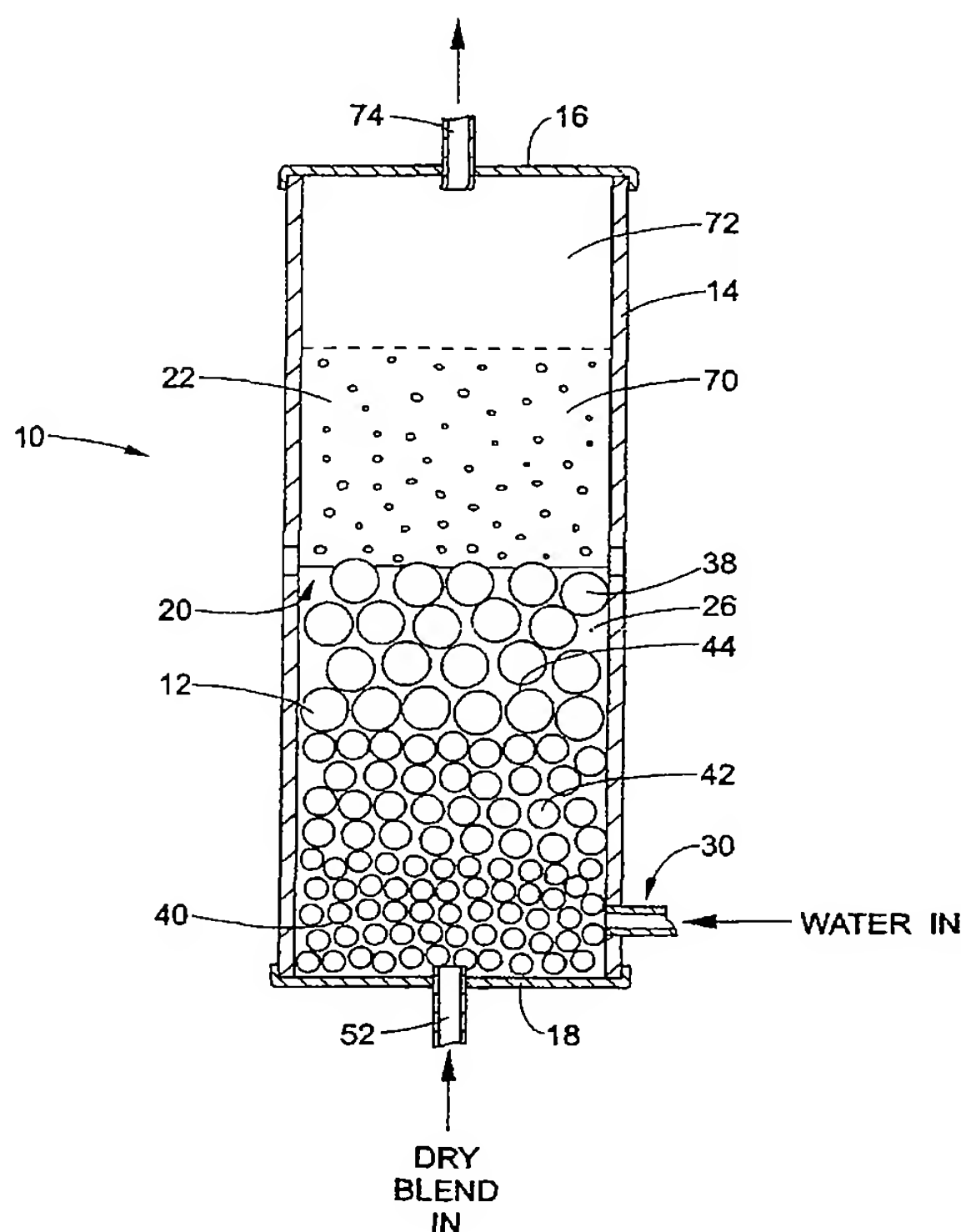
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[Continued on next page]

(54) Title: HUMIDIFICATION OF HYDROCARBON MIXTURES FOR USE IN POLYMER SYNTHESIS



(57) Abstract: A humidification system (A) for humidifying a dry hydrocarbon stream includes a column (10) which defines an interior cavity (20). The cavity is partially filled with a bed (12) of a packing material (40) and a layer of water (20), leaving a headspace above the water. An inlet (52) adjacent a lower end of the cavity receives a dry hydrocarbon stream which is broken up by the packing material and dissolves water as it passes therethrough. Entrained water droplets fall out of the wet blend in a disengagement zone (70) above the water layer leaving the hydrocarbon stream humidified yet substantially free of liquid water in an upper region (72) of the column.

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**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## HUMIDIFICATION OF HYDROCARBON MIXTURES FOR USE IN POLYMER SYNTHESIS

### BACKGROUND OF THE INVENTION

The present invention relates to humidification of hydrocarbons, such as butadiene, prior to polymerization and will be described with particular reference thereto. The process is also applicable to other fluids in which water is poorly soluble, however.

Polymerization of 1,3-butadiene to form *cis*-1,4-polybutadiene with the aid of Ziegler-Natta type catalyst systems is known. The presence of controlled amounts of water in certain such polymerizations has been found to have a beneficial effect on the activation of the catalyst. In particular, small amounts of dissolved water, of the order of 10 to 200 ppm, have been found to be beneficial to catalytic activity.

Water may be introduced by a dispersion in the reactants themselves or in the solvent(s). In one method, water is passed through a porous frit material into a stream of the hydrocarbon mixture. In other methods, water is introduced to the polymerization reactor. Another method of introducing water employs a cyclone. However, the presence of free water in liquid form in the polymerization reactor can inactivate the catalyst rather than assist in its activation. Prior methods of incorporating water have often resulted in the presence of water droplets in the hydrocarbon feed.

The present invention provides a new and improved apparatus and method for humidification of a hydrocarbon, which overcomes the above-referenced problems and others.

### SUMMARY OF THE INVENTION

The invention provides a method of humidifying a hydrocarbon stream wherein the stream is passed through a bed including a packing material and water. The result is a humidified hydrocarbon stream having

water dissolved therein. (Dissolved indicates a lack of unassociated, entrained water in liquid form such as, e.g., droplets.)

In another aspect, an apparatus for humidifying a hydrocarbon stream is provided. The apparatus includes a vessel which defines an interior cavity. A bed of a packing material is disposed in the cavity. Water fills at least a portion of the bed. An inlet adjacent, e.g., a lower end of the cavity receives a hydrocarbon stream.

The hydrocarbon stream resulting from this process and apparatus is humidified but is essentially free of liquid water. Additionally, the level of water in (i.e., humidification of) the hydrocarbon stream may be controlled.

#### BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a schematic view of a system for humidifying hydrocarbons according to the present invention.

FIG. 2 is a side sectional view of the column of FIG. 1.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

In FIGURE 1, a system **A** for humidifying a hydrocarbon stream is shown. The system dissolves water in the hydrocarbon stream at or below its saturation limit and ensures that little or no free (i.e., undissolved) water exists in the final process stream as water droplets. The hydrocarbon stream can be a single hydrocarbon in liquid or gaseous form or a mixture of hydrocarbons, such as a reactive monomer in an inert solvent.

Exemplary hydrocarbon monomers include mono-unsaturated alkenes such as ethene, propene, butene, etc.; conjugated dienes such as butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, and the like; and styrene and its derivatives, and combinations thereof. The system is particularly useful for hydrocarbon monomers in which water is poorly soluble, such as butadiene.

Suitable solvents include aliphatic, aromatic, or cycloaliphatic hydrocarbons, examples of which are butane, pentane, hexane, toluene,

benzene, cyclohexane, and the like. In one embodiment, the hydrocarbon stream includes a mixture of butadiene and hexane in a ratio of from 1:0 (i.e., pure butadiene) to 1:20.

In an alternative embodiment, one or more components of a hydrocarbon stream is humidified and then mixed with other component(s) of the stream downstream of the column **10**. This is particularly preferred when one of the components of the hydrocarbon stream has a lower water saturation level than the others. When relatively high water concentrations are desired, the component having a poor water solubility may be omitted from the hydrocarbon(s) to be humidified and added to the humidified component(s) prior to processing. For example, in the case of butadiene and hexane, butadiene has a saturation level of around 700 ppm at room temperature while hexane has a saturation level of around 200 ppm. Butadiene may be humidified alone to a water content of, for example, above 200 ppm prior to hexane being added to the humidified butadiene. Preferably, the butadiene is humidified to a level below that at which water drops out of the combined butadiene/hexane mixture once the hexane is added.

The hydrocarbon stream leaves the system with dissolved water up to the saturation limit of the hydrocarbon stream. For example, a hexane-butadiene mixture may be saturated up to about 200 ppm water, depending on the composition of the stream.

With reference also to FIGURE 2, dissolution of water in the hydrocarbon stream may take place in a cylindrical column **10** packed with a bed **12** of a dispersion material. Column **10** is formed from a structural material, preferably a non-reactive metal such as steel, and has a cylindrical side wall **14** closed at upper and lower ends by flanges **16**, **18**. Bed **12** partly fills an interior **20** of the column, preferably about the lower half, leaving a head space **22** which is free of the dispersion material.

A water zone **26** fills the column interior approximately up to the top of the dispersion material, i.e., approximately the lower half of the column, and fills the voids in column packing bed **12**. Preferably, the water covers

the packing material although the water level may drop during humidification process such that the packing material becomes only partially covered by the water. The water, which is preferably distilled or otherwise purified, can be introduced to the column through an inlet line **30** adjacent the lower end of the column. A liquid level gauge **32** can be used to adjust the height of the water to the desired level. Once the desired water level is achieved, a valve **34** in the inlet line is closed and the column is ready to receive the hydrocarbon stream. The valve may be a non-return valve, or have a non-return valve **36** associated therewith for inhibiting backflow from the column.

The bed **12** is preferably formed from small particles or beads **38** (not shown to scale) formed of an inert material, such as porcelain. Preferably, the beads are spherical in shape, although other configurations are also contemplated. In a preferred embodiment, the beads range in diameter from smaller at the bottom to slightly larger at the top of the bed. As shown in FIGURE 2, this size configuration can be achieved using a lower layer **40**, in which the beads have a diameter of from about 0.2 to about 0.4 cm, an intermediate layer **42** in which the beads have a diameter of from about 0.5 to about 0.8 cm, and upper layer **44** with about 1.0 to about 1.5 cm diameter beads. Alternatively, the beads may be of the same size throughout the column. Bead size and arrangement can depend on factors such as the height of the column and desired flow rate through bed **12**.

In this exemplary embodiment, the column is about one 1 m in height and 10-20 cm in diameter; beads occupy the lower 40-50 cm. The smaller the beads and the higher the bed, the greater the reduction in flow rate. However, smaller beads tend to break up the hydrocarbon stream into droplets more quickly. Thus, a compromise between the size of the beads and the desired flow rate must be made. An exemplary bead size ranges from about 0.2 to 1.5 cm expressed in average bead diameter.

The hydrocarbon stream is introduced to the column interior through an inlet line **50** via an inlet port **52** in the lower flange **18**. The hydrocarbon stream is preferably introduced as a dry blend. By "dry" it is meant that the

hydrocarbon or blend is essentially free of water. However, the blend can contain water, as dissolved water and/or water droplets, because the water droplets where present are advantageously removed by the system.

A pump **54**, such as a gear pump in the inlet line, pressurizes the dry blend to a pressure of about  $10 \text{ kg/cm}^2$ . Excess pressure may be relieved through a pressure relief valve **56** which is set at just below the maximum pressure desired, e.g., about  $13 \text{ kg/cm}^2$ . A valve **60** in the inlet line **50** may be closed or adjusted to reduce or stop the flow of the hydrocarbon stream into the column. A non-return valve **62** prevents backflow of the stream to its source **64**.

The entering hydrocarbon stream passes through the water and packed bed **12**. The dispersion material breaks the stream into numerous narrow pathways and provides a high surface area of contact between the hydrocarbon stream and the water. The hydrocarbon stream is rapidly broken into small droplets that come into contact with the surrounding water, dissolving a portion of the water into each droplet. The hydrocarbon, being lighter than the water, continues upwards into a disengagement zone **70**, above the water layer. In this zone, any undissolved, entrained water falls back down into the bed, due to its higher density. The hydrocarbon droplets coalesce in the upper region **72** of the disengagement zone **70** and exit the column through an outlet **74** as a single hydrocarbon phase, which is substantially free of water droplets but contains the desired dissolved water. The disengagement zone **70** is thus preferably of sufficient height to allow the separation of entrained water and hydrocarbon to occur. Alternatively, a separate chamber is used for separating the entrained water droplets from the hydrocarbon stream.

Optionally, a portion of the resulting wet hydrocarbon stream may be recycled back to the bottom of the column via a recycle line **80** for another pass through the column (see FIGURE 1). The pump **54** can be used to control the proportion returning to the column. Recycling the hydrocarbon stream in this way ensures that the wet hydrocarbon stream in the column is



saturated with water and tends to ensure that a more stable water content value is achieved. The portion which is recycled can vary depending on the flow rate of the hydrocarbon and the solubility of water in the hydrocarbon. At relatively low flow rates, particularly where the desired water concentration is less than the maximum achievable saturation limit, a single pass has been found to be adequate. At higher flow rates, 50% or more of the hydrocarbon stream may be recycled through the column. A non-return valve **82** in the return flow line **80** ensures that the fluids maintain the direction of flow as shown in FIGURE 1.

The exiting wet hydrocarbon blend may be mixed with additional dry blend to achieve a desired dissolved water content, although other methods of combining the two streams are also contemplated. FIGURE 1 shows a static mixer **90** which combines wet and dry streams. For example, the water content may be reduced to 50% or 20% of the saturation limit by appropriate mixing of wet and dry blend streams. Specifically, a portion of the dry blend from the inlet line is fed via a direct line **92** to the mixer where it is mixed with the wet blend from the column. A valve **94** adjusts the portion of the dry blend which passes directly to the static mixer. The dry blend passing to the static mixer is preferably of the same hydrocarbon composition as that passing through the humidification column **10**, although the dry blend can have a different hydrocarbon composition. If a fully water-saturated hydrocarbon stream is required, the step of mixing with a portion of the dry blend may, of course, be eliminated.

The mixed stream, i.e., a humidified blend, having a lower water content than the wet blend from the column, exits the mixer via an outlet line **96** which transports the humidified blend to a site **98** at which it is to be utilized, such as a polymerization reactor. Such reactors are disclosed in, for example, U.S. Patent No. 4,472,559 to which the reader is referred for more detail.

A moisture probe **100**, fluidly coupled with the outlet line **96**, detects the moisture content of the humidified blend and signals a moisture analyzer



**102.** The moisture analyzer provides an indication of the moisture level of the humidified blend. An operator may manually adjust the control valve **94** to set the ratio of dry to wet fraction or the control valve **94** may be adjusted automatically using a process loop controller **106**, integral with or separate from the moisture analyzer **102**, whose process variable input is the moisture level and whose output drives the control valve position. In this way, a desired output moisture level may be maintained.

Moisture probe **100** may be positioned directly in the outlet line **96** from the static mixer or, as shown in FIGURE 1, may be positioned in a separate sampling chamber **110** into which a portion of the humidified blend is directed periodically for evaluation. In the embodiment of FIGURE 1, a 3-way valve **112** in the outlet line is operated periodically to pass a sample of the humidified blend into the sampling chamber **110** through a sampling line **114**. Optionally, a heater **118** in the sampling line heats the sample to a sufficient temperature to lower the relative humidity of the analyzed blend and thereby maintain the integrity of probe **100**. Water, which falls out of the humidified blend in the chamber, is carried out of the bottom of the chamber via a drain line **120** by periodically opening a drain valve **122**.

The sampled humidified blend may be returned to the outlet line **96** or passed out of the sampling chamber **110** to a waste line **120** via valve **122**. Alternatively, the sample may be returned to the column and mixed with the incoming dry blend.

After a sampling operation is complete, the sampling chamber **110** may be flushed with a dry fluid such as a dry hexane to remove traces of moisture from the chamber. For this purpose a 3-way valve **136** in the sampling line **114** is operated with the waste valve **122** open to carry the dry hexane purge through the sampling line and through the chamber **110**, carrying any remaining wet hydrocarbon out of the chamber through the waste line **130**. When another moisture determination is to be made,

hexane is flushed from the chamber by passing a portion of the wet blend through the chamber until the moisture content is stabilized.

The system shown is designed for periodic sampling of the wet blend and for the subsequent draining and flushing of the moisture probe in an effort to maintain probe integrity, accuracy and longevity during process monitoring. The composition and construction of the moisture probe make it typically sensitive to high moisture levels and to process streams with high saturation levels. Using the probe for intermittent monitoring and by flushing the probe with dry solvent can maintain a long probe life and helps to maintain the probe within its current calibration.

The system may include additional valves and regulators for regulating flow through the system, such as a pressure regulating valve **140** in the outlet line which maintains the humidified blend and column at a positive pressure. This may be associated with a pressure transducer **142** for detecting the pressure in the outlet line. Other pressure transducers may be provided, for example, at **144**, **146**, **148**, and **150**. Other valves may be provided, such as a wet blend sampling valve **152**, which allows a sample of the wet blend to be withdrawn from chamber **110** through a line **156** for analysis. A valve **158** may also be provided for closing off a line **160** between the chamber **70** and the liquid level gauge **32**. A supplementary pressure relief valve **162** may be provided in a portion **164** of the inlet line, which carries both dry blend and recycled wet blend to the chamber. A valve **170** for closing off the line between the humidification system and the polymerization reactor may also be provided.

For a column of the dimensions described above, flow rates of the humidified blend of about 20 to about 50 L/hr or more are readily achieved. Obviously, greater flow rates may be achieved with larger columns.

When the water level in the column drops below a selected minimum level, typically just above the top of the dispersion material, the valve **34** is opened again to allow more water into the column. During water addition,

valve **60** may be closed. In this way, the system can be run relatively continuously for long periods of time.

The humidified hydrocarbon stream may be used as a process stream in a polymerization reaction which relies on the presence of small amounts of dissolved water to activate a catalyst for the polymerization reaction, such as the production of high *cis*-content polybutadiene with Ziegler Natta-type catalysts, such as those incorporating aluminum alkyls, alkyl chlorides, or aluminum alkoxides with a transition element, such as Co or Ni. Alternatively, or additionally the humidified hydrocarbon stream may be used for *in situ* generation of catalyst systems, for example, the preparation of alkyl aluminoxanes such as methyl aluminoxanes. This avoids the need to prepare the catalyst system in advance and store it in a hydrocarbon carrier liquid.

The following example demonstrates the effectiveness of the humidification system.

#### EXAMPLE

Three layers of porcelain beads occupying the lower 40 cm of a 1 m-tall column (a lower layer **40** of a bead diameter of about 0.3 cm, an intermediate layer **42** of a diameter of about 0.6 cm, and an upper layer **44** of a diameter of about 1.3 cm) was filled about 50% with water. The pressure in the inlet line **50** was maintained at 10.5 kg/cm<sup>2</sup>. A dry, 15% mixture of butadiene in hexane was fed to the column. The control valve **94** was opened at about 50% to mix about 50% dry blend with the wet blend exiting from the column. A flow rate of 22-45 L/hr. of a humidified blend containing a well-controlled 100 ppm moisture at an outlet pressure of 10 kg/cm<sup>2</sup> was achieved.

We claim:

1. A method of humidifying a stream of one or more hydrocarbons, said method comprising passing the hydrocarbon stream through a bed comprising a packing material and water, thereby forming a humidified hydrocarbon stream, said hydrocarbon stream optionally further comprising a solvent in which said one or more hydrocarbons is soluble.
2. The method of claim 1 wherein the packing material is in the form of particles or beads, said particles or beads optionally being spherical.
3. The method of claim 1 wherein said hydrocarbon stream passes upwardly through said bed.
4. The method of claim 3 wherein said packing material comprises particles, said particles having a smaller average diameter adjacent the bottom of said bed than adjacent the top thereof.
5. The method of claim 4 wherein said particles nearer the bottom have an average diameter of 0.2 to 0.5 cm and said particles nearer the top layer have an average diameter of 1 to 1.5 cm.
6. The method of any of claims 1 to 5 wherein said hydrocarbon stream includes butadiene.
7. The method of claim 6 wherein said solvent comprises hexane.
8. The method of any of claims 1 to 7 further comprising, after the step of passing the hydrocarbon stream through the bed, allowing liquid water to fall out of the humidified hydrocarbon stream in a head space above the bed so that said humidified hydrocarbon stream is substantially free of undissolved water.

9. The method of any of claims 1 to 8 further comprising combining said humidified hydrocarbon stream with a second portion of a hydrocarbon stream to achieve a desired moisture content.

10. The method of claim 9 wherein said humidified hydrocarbon stream includes 200 ppm water and the step of combining said humidified hydrocarbon stream with a second portion of a hydrocarbon stream results in a combined hydrocarbon stream having a moisture content of from 10 to 150 ppm.

11. The method of any of claims 1 to 10 further comprising recycling at least a portion of said humidified stream through said bed.

12. An apparatus for humidifying a hydrocarbon stream comprising:
- a) a vessel which defines an interior cavity, said vessel comprising an inlet adjacent a lower end of the cavity for receiving a hydrocarbon stream and, optionally, a second inlet for adding water to said vessel;
  - b) a bed in the cavity, said bed comprising a packing material and water which fills at least a portion of the bed;
  - c) optionally, a return line for returning to the cavity a portion of a hydrocarbon stream which has been humidified;
  - d) optionally, a mixer for mixing said humidified hydrocarbon stream with an unhumidified hydrocarbon stream to form a combined stream; and
  - e) optionally, a sensor for detecting a moisture content of at least one of the unhumidified hydrocarbon stream and the combined stream.

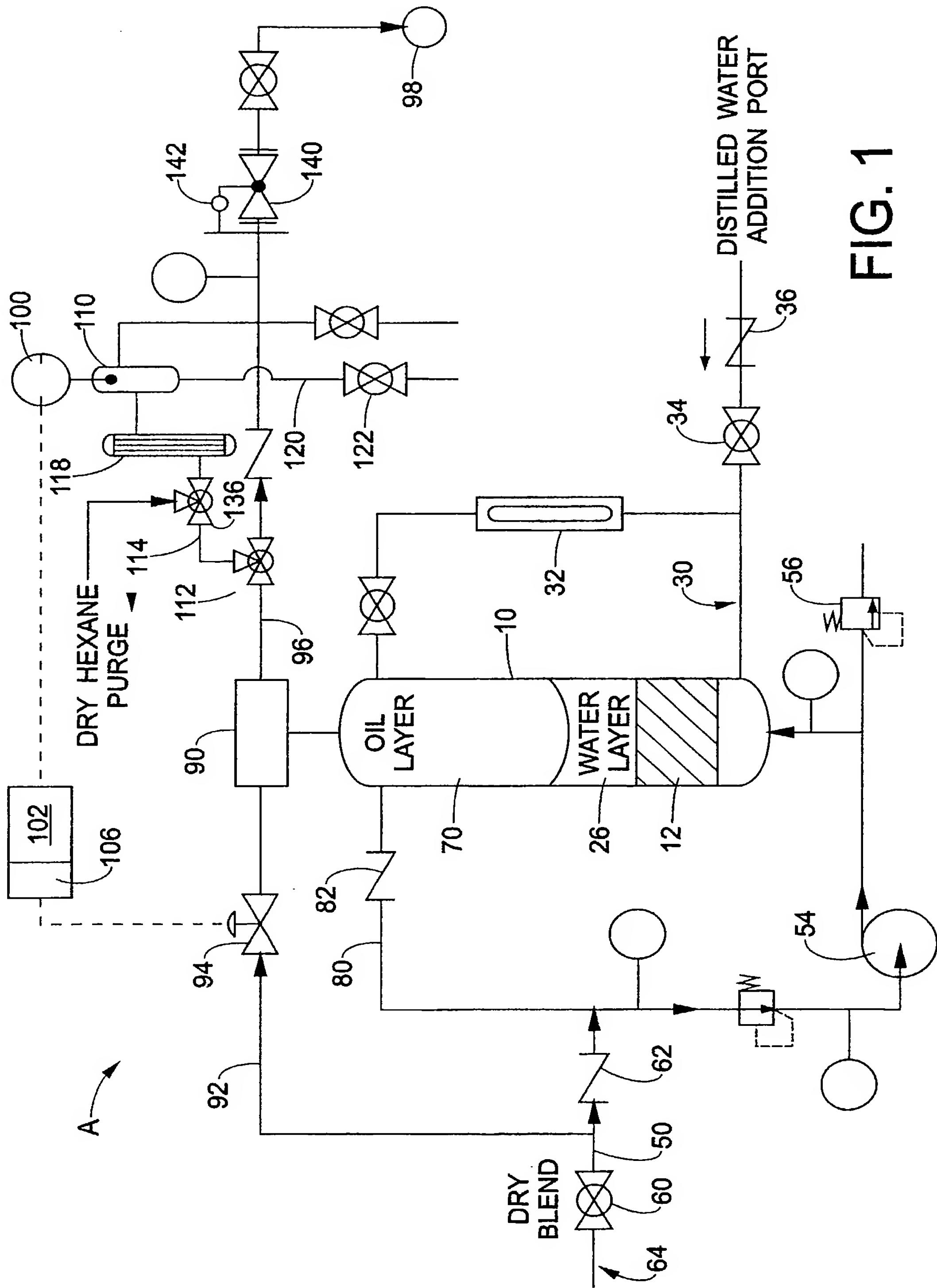


FIG. 1



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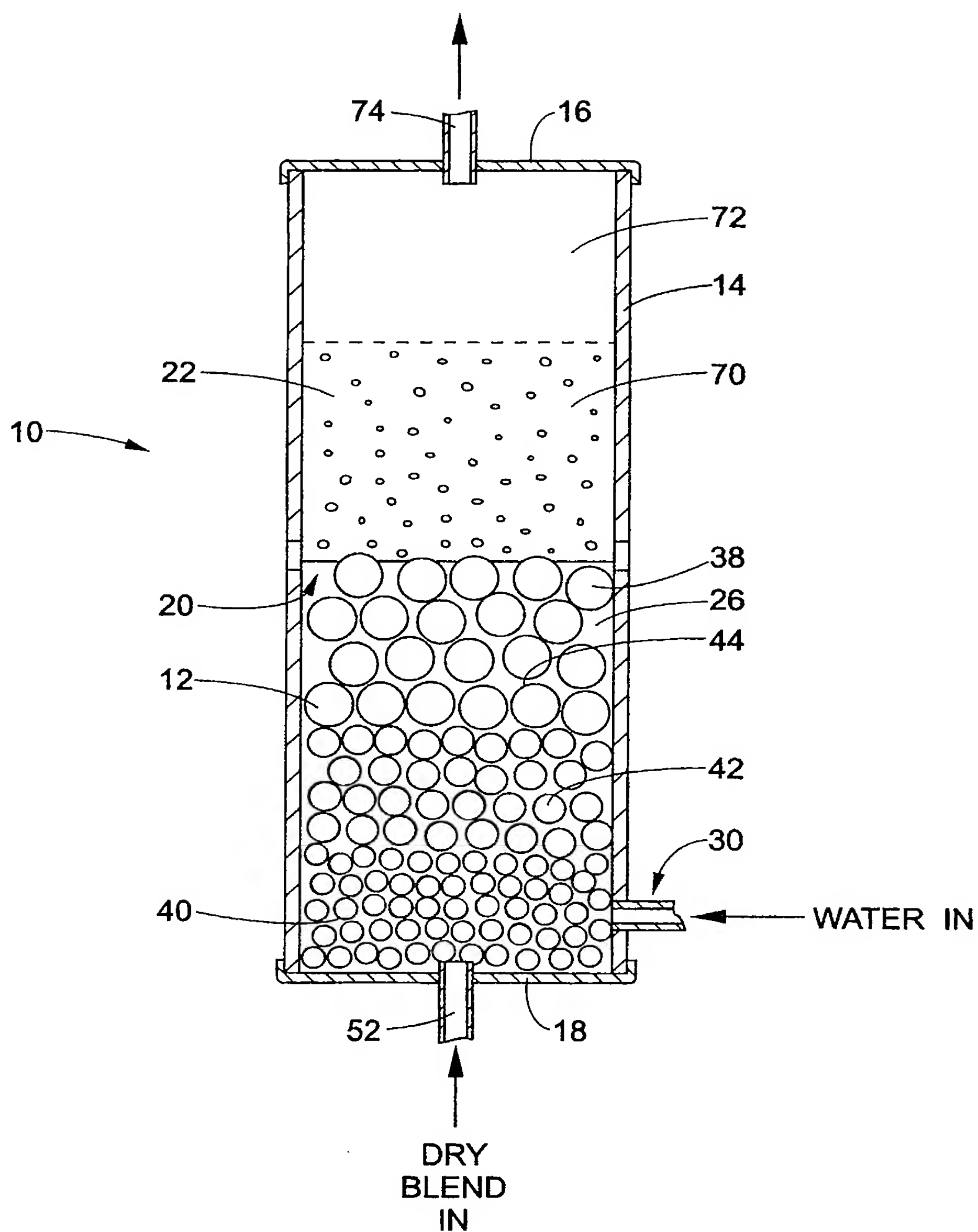


FIG. 2

SUBSTITUTE SHEET (RULE 26)

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 02/06478

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C07C11/167 B01F5/06

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
WPI Data, EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 225 199 A (LOMBARD JACQUES) 8 November 1974 (1974-11-08) claims ---	12
X	FR 2 321 318 A (BAYER AG) 18 March 1977 (1977-03-18) figure -----	12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*G\* document member of the same patent family

Date of the actual completion of the international search

4 July 2002

Date of mailing of the international search report

17/07/2002

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/06478

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-5,8-11 (all in part)  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-5,8-11 (all in part)

Present claim 1 relates to an extremely large number of possible hydrocarbons and solvents. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the hydrocarbons and solvents claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the hydrocarbon of claim 6 (butadiene) and the solvent of claim 7 (hexane).

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/06478

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2225199	A	08-11-1974	FR 2225199 A1	08-11-1974
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